Spin dynamics of hole doped Y_2BaNiO_5

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(Received February 1, 2008)

Starting from a multiband Hamiltonian containing the relevant Ni and O orbitals, we derive an effective Hamiltonian H_{eff} for the low energy physics of doped Y_2BaNiO_5. For hole doping, H_{eff} describes O fermions interacting with S=1 Ni spins in a chain, and cannot be further reduced to a simple one-band model. Using numerical techniques, we obtain a dynamical spin structure factor with weight inside the Haldane gap. The nature of these low-energy excitations is identified and the emerging physical picture is consistent with most of the experimental information in $Y_{2-x}Ca_xBaNiO_5$.

The properties of antiferromagnetic (AFM) chains have been a major topic in the study of low dimensional magnetism. Haldane's conjecture about the existence of a gap in spin S=1 one dimensional (1D) Heisenberg systems[1] has inspired a considerable amount of research[2–4]. Recently, there has been wide interest in Y_2BaNiO_5, a near ideal realization of the S=1 AFM Heisenberg chain[5], and the effects of different dopants on specific heat[6] and magnetic properties[7,8]. While replacement of Ni^{2+} (S=1) by non-magnetic Zn^{2+} or Mg^{+2} simply cuts the spin chains, the replacement of off-chain Y^{3+} by Ca^{2+} introduces holes primarily on oxygen sites[7]. In the last case, resistivity decreases by several orders of magnitude, and inelastic neutron scattering reveals new states inside the Haldane gap[7]. In addition, the magnetic behavior of the Ca doped system, markedly different from the Mg-doped one, is spin-glass like with a characteristic temperature $T_g \sim 2K$.[8]

It has been shown that spin models with localized site or bond impurities lead to in-gap states for certain parameters[9,10]. While the results are interesting, these models can only be valid for completely localized added holes, which seems not to be the case in $Y_{2-x}Ca_xBaNiO_5$[7]. Models for mobile holes have been studied[11,12], but with effective hole hopping t more than one order of magnitude smaller than realistic values[13]. In Ref.[12], the essential physics is reduced to that of a weakly mobile S=1/2 spin (representing a "Zhang-Rice" doublet[12,18]) with exchange interaction $J' = 0$ with its nearest-neighbor (NN) Ni spins. In the static limit, this model is known to lead to a bound state inside the Haldane gap when J' is weak[9,10]. However J' results strong and ferromagnetic (FM)[19] and, in agreement with Ref.[10], we find no bound states in this static case. Thus, the origin of the observed states inside the Haldane gap in $Y_{2-x}Ca_xBaNiO_5$[7] is not yet clear.

In this Letter, we start from a multiband Hamiltonian H_{mb} for NiO_5 linear systems, containing all essential orbitals and interactions. An effective low-energy Hamiltonian H_{eff} is derived. By exact diagonalization of H_{eff}, we provide an explanation of the observed inelastic neutron spectrum[7]. In addition, our results are consistent with the measured gap, x-ray absorption spectrum[7], magnitude of the intra- and inter-chain exchange[5], magnetic susceptibility and muon spin relaxation[8].

The starting Hamiltonian is the extension to the 1D NiO_5 system of the one used by van Elp *et al.*[20] for a NiO_6 cluster, restricting the basis of Ni orbitals to the $3d_{3z^2-r^2}$ and $3d_{x^2-y^2}$ (z is the direction along the chain):

$$H_{mb} = \sum_{i\alpha} \epsilon_i c_{i\alpha\sigma}^\dagger c_{i\alpha\sigma} + \sum_{i\neq j\alpha\sigma} t_{ij}^{\alpha\beta} c_{i\alpha\sigma}^\dagger c_{j\beta\sigma}$$
$$+ \sum_{i\alpha}(U_i + \frac{J_i^H}{2})n_{i\alpha\uparrow}n_{i\alpha\downarrow}$$
$$+ \sum_{i\alpha\neq\beta\sigma\sigma'}(U_i - \frac{3J_i^H}{4})n_{i\alpha\sigma}n_{i\beta\sigma'}$$
$$+ \sum_{i\alpha\neq\beta}J_i^H(c_{i\alpha\uparrow}^\dagger c_{i\alpha\downarrow}^\dagger c_{i\beta\downarrow}c_{i\beta\uparrow}/2 - \mathbf{S}_{i\alpha}\cdot\mathbf{S}_{i\beta})$$
$$+ \sum_{i\neq j\alpha\beta\sigma\sigma'}U_{ij}n_{i\alpha\sigma}n_{j\beta\sigma'}, \qquad (1)$$

where $c_{i\alpha\sigma}^\dagger$ creates a hole with spin σ on the orbital α of site i. The interactions included are the on-site Ni repulsion U_d, Ni Hund interaction J^H (for O sites $J_i^H = 0$), O on-site repulsion U_p and Ni-O NN repulsion U_{pd}, for the six O atoms surrounding a Ni one. For simplicity, the basis of O orbitals considered is reduced to the $2p_z$, and the two linear combinations of $2p$ orbitals lying in the xy plane having optimum hybridization with their NN Ni orbitals (the amount of other O $2p$ states, in the low energy manifold, is of the order of 1%). From atomic data we obtain $J^H = 1.6$eV. From Ref.[20] $U_d = U(^2E_g) = 10$eV. The values of $U_p = 4$eV and $U_{pd} = 1.2$eV were taken from Ref.[14]. The hopping parameters were taken from

Ref.[20], scaling the Ni-O (O-O) hoppings with an $r^{-7/2}$ (r^{-2}) law, and multiplying them by a common factor f. Finally, f and Δ, the energy necessary to take a hole from Ni^{2+} and put it in any of the six nearest O^{2-} ions, were chosen to give $J = 0.023$eV and a charge transfer gap $E_g = 1.84$eV[21] in agreement with experiments[7].

The resulting values $f = 0.85$ (implying a $3d_{3z^2-r^2} - 2p_z$ hopping of 1.61eV) and $\Delta = 7.4$eV are reasonable taking into account that Δ should increase to the left of the periodic table, and $\Delta = \epsilon_p - \epsilon_d + U_{pd} \sim 4.8$eV in the cuprates[14]. To gain further confidence on the resulting parameters, we have compared other two quantities with experiment. Solving exactly H_{mb}, including the repulsion V_d (V_p) between a Ni $2p_{3/2}$ core hole and a Ni $3d$ (NN O $2p$) hole in a NiO_6 cluster, we have calculated the shift towards lower energy in the Ni L_3 x-ray absorption spectrum in going from polarization along the chain to a perpendicular one. Taking $V_d - V_p$=10eV[14] we obtain 0.80eV, while the experimental shift is 0.91eV[7]. We have also calculated the exchange along b direction (perpendicular to the chains) J_b, starting from the exact solution of two NiO_6 clusters, and treating the hoppings connecting the two clusters with the cell-perturbation method[15]. We obtain $J_b = 0.173K = 6.4 \times 10^{-4}J$, near the upper bound $5 \times 10^{-4}J$ estimated in Ref.[5].

The low-energy reduction procedure[14−16,22] which we found most convenient for the present problem is the one used successfully in Ref.[22] to reproduce low-energy photoemission and magnetic properties of the three-band model for the cuprates. The *form* of the low-energy effective Hamiltonian H_{eff} is determined by a canonical transformation. For hole doping H_{eff} has the form of a spin-fermion H_{sf}(or Kondo-Heisenberg) model as in Ref.[11]. For electron doping, H_{eff} has the form of a one-band model H_{1b} (Eq. (3) with $J' = 0$ and $t = -0.351eV$). The procedure eliminates linear terms in the Ni-O hopping, retaining second order contributions and the fourth-order exchange J. However, the *values* of the parameters are determined fitting the energy levels of H_{sf} to the corresponding ones of H_{mb} in conveniently chosen clusters (Ni_2O_{11} for electron-doped and NiO_6 for hole-doped systems). H_{sf} can be written as:

$$H_{sf} = \sum_{i\delta\sigma} p^\dagger_{i+\delta\sigma} \, p_{i-\delta\sigma} \left[(t_1 + t_2) \left(\mathbf{S}_i \cdot \mathbf{\Sigma}_{i-\delta} + \frac{1}{2} \right) - t_2 \right]$$
$$+ J_K \sum_{i\delta} \left(\mathbf{S}_i \cdot \mathbf{\Sigma}_{i+\delta} - \frac{1}{2} \right)$$
$$+ \frac{J}{2} \sum_{i\delta} \mathbf{S}_i \cdot \mathbf{S}_{i+2\delta} + \frac{\epsilon}{2} \sum_{i\delta\sigma} p^\dagger_{i+\delta\sigma} \, p_{i+\delta\sigma} \quad (2)$$

Here i labels a Ni site, and $i + \delta$ denotes its two NN O atoms along the chain, $p^\dagger_{i+\delta\sigma}$ creates an *effective* $2p_z$ hole (it contains information of other Ni and O orbitals) of spin σ at site $i + \delta$, and $\mathbf{S}_i$ ($\mathbf{\Sigma}_{i+\delta}$) is an effective spin 1 (1/2) at site i ($i + \delta$). We obtain $t_1 = 0.64$eV, $t_2 = 0.89$eV and $J_K = 1.40$eV; $\epsilon = 8.97$eV is irrelevant for the spin dynamics, but determines the charge gap[21].
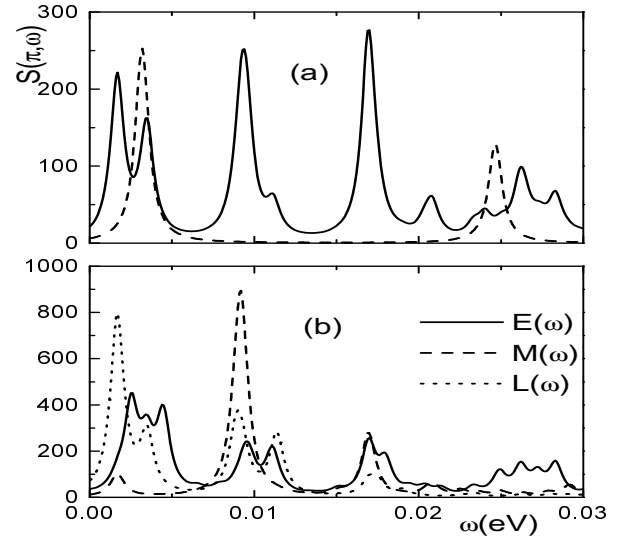

FIG. 1. (a) Full (dashed) line: dynamic structure factor $S(\omega,\pi)$ ($S(\omega,\pi)/5$)of $O(NiO_5)_{10}$ system with open boundary conditions and one (zero) added hole. (b) Correlation functions $E(\omega)$, $M(\omega)$ and $L(\omega)$ defined in the text.

In Fig.1(a) we show the dynamical structure factor $S(q,\omega) = \frac{1}{3} \int e^{i\omega t}dt \, \langle \mathbf{S}_q(t).\mathbf{S}_{-q}(0) \rangle$ at wave vector $q = \pi$, in a $(NiO_5)_{10}O$ system with one added hole described by H_{sf}, using open boundary conditions (OBC), and compare it with the result for the undoped system. At first sight, OBC appears to be an inconvenient choice for studying states inside the Haldane gap, since an open chain has always low-energy spin excitations associated with the nearly free spins at the ends[2,4,12]. However, the use of periodic BC leads to spurious low-energy excitations due to the *frustration* generated by effective FM interactions introduced by the hole dynamics. This is particularly clear when the spin-spin correlation between the ends of the open chain is FM. Hence, we used OBC and identified the excitations related to the end states by the dynamical response of the system to a staggered magnetic field decaying exponentially along the chain. For no added holes, $S(\pi,\omega)$ shows a peak at energy $\omega \sim J = 23$meV corresponding to the Haldane gap (shifted from $\omega \sim 0.4J$ due to the finite size of the chain[4]), and a peak at $\omega \sim 3$meV corresponding to excitations localized at the ends of the chain. This is the behavior expected for Zn or Mg doping. $S(\pi,\omega)$ for one added hole (representing the Ca doped system) is markedly different. The Haldane peak shifts to lower energy, its intensity decreases, and significant spectral weight appears near the middle of the Haldane gap. Both features are in agreement with experiment[7]. Among the three peaks below the Haldane gap, the second one lies nearly at the same energy as that of the low energy peak of the undoped system. One would then suspect that it is mainly related with the ends of the chain and it should disappear in the

thermodynamic limit, since Ca doping does not break the chains. This suspicion is confirmed by inspection of the correlation function $E(\omega) = \int dt \ e^{i\omega t} \langle \frac{1}{2} | O(t)O(0) | \frac{1}{2} \rangle$ where $O = \sum_j e^{-j(1+i\pi)} S_j^z$ and $|m\rangle$ is the component with $S^z = m$ of the $S=3/2$ ground state. $E(\omega)$ measures the response of the system to an excitation localized at one end of the chain. The result is shown in Fig.1(b). There is an intense structure around 3meV consisting of three peaks. The first and the third one are practically absent in $S(\pi, \omega)$ for symmetry reasons. The second corresponds precisely to the second peak of $S(\pi, \omega)$.

What is the origin of the other two peaks below the Haldane gap? Guided by the wave function of the ground state and the first few excited states, we have looked for dynamical correlation functions with large intensity at these peaks to unravel their nature. The peak at 9meV (near the middle of the Haldane gap) is related to a smaller effective magnetic interaction between the Ni spins at a distance of one lattice parameter and a half from the O hole and their NN Ni spins. To check this and since the O hole tends to be localized near the middle of the chain, we have calculated $M(\omega) = \int dt \ e^{i\omega t} \langle \frac{3}{2} | O_2(t)O_2(0) | \frac{3}{2} \rangle$ with $O_2 = \sum_{|j-c| \geq 3/2} (-1)^j e^{\frac{3}{2} - |j-c|} S_j^z$, where the half-integer c denotes the center of the chain. As shown in Fig.1(b), $M(\omega)$ has only an intense peak at 9meV, and a smaller contribution at the Haldane peak. Replacing O_2 by $S_{c+5/2}^z - S_{c-5/2}^z$, the corresponding dynamical correlation function $L(\omega)$ has an intense peak only at the energy (around 1.7meV) of the lowest peak in $S(\pi, \omega)$, and smaller contributions at the other low-energy peaks (see Fig.1 (b)). Note instead that the responses to the end excitation $E(\omega)$ and to the excitation peaked at the middle of the Haldane gap $M(\omega)$ have negligible contributions at 1.7meV. The energy of the lowest possible excitation depends non-monotonically on system size (for example it lies at 0.6meV for $O(NiO_5)_8$), but we find always an excitation at very low energies. These results suggest the presence of weak magnetic links near the O hole and the presence of a FM polaron which is a bounded state between the charge and a local magnetic excitation. The origin of this polaron, can be described as follows: the large values of t_1, t_2, and J_K (relative to J) tend to stabilize a doublet between an effective Ni spin at any site i and a hole in the orbital $p_{i+\delta} + p_{i-\delta}$ ("Zhang-Rice" doublet (ZRD))[12,18], and induces a residual FM interaction between the ZRD and its NN Ni spins[19]. This FM interaction can be interpreted in terms of a NN attractive interaction between the ZRD and a magnetic excitation. This attractive interaction gives place to a bound state (small polaron) with a binding energy which is a fraction of J. Within this picture, the effect of the operator $M(\omega)$ is to make a spin excitation *inside* the polaron, while the effect of $L(\omega)$ is to make an excitation in the spin which is *beside* the polaron. It is clear that the AFM interaction between the latter spin and the one inside the polaron must be reduced, giving place to a weak link, by

the effects of t_1, t_2, and J_K which tend to polarize the spin background. This explains the origin of the very low-energy excited state, generated by the application of $L(\omega)$ to the ground state.

We discuss briefly a further reduction of H_{sf} to a *simple*[23] one band Hamiltonian H_{1b}, since in general, it is successful in the case of the cuprates[14–16,22]. The low-energy physics is dominated by "Zhang-Rice" doublets. The overlap of some of these many body states is too large (1/3 compared with 1/8 in the case of the cuprates[16]) rendering cumbersome to obtain H_{1b} as an expansion in powers of the overlap[16]. We then construct orthogonal Wannier functions π_i at each Ni site, write H_{sf} in this basis using $p_{i+\delta} = (2/\pi) \sum_n (-1)^{n+1} (2n - 1)^{-1} \pi_{i+n,\sigma}$, calculate $P_1 H_{sf} P_1$ (P_1 is a projector over local orthogonal Zhang-Rice doublets), and map it into H_{1b}[16]. Unfortunately, contrary to the case of the cuprates[16], P_1 does not commute even approximately with H_{sf} in any limit. Local quadruplets are important in the low energy physics[23]. Assuming for simplicity $J_K = t_1 + t_2$, and including only the two largest terms (besides J) we obtain:

$$H_{1b} = \sum_{j\delta} \left[t \, P_{j,j+2\delta} \left(\widetilde{\mathbf{S}}_j \cdot \mathbf{S}_{j+2\delta} + \frac{1}{2} \right) - J' \, \widetilde{\mathbf{S}}_j \cdot \mathbf{S}_{j+2\delta} \right] \quad (3)$$
$$+ J \sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1}$$

Here j runs over the positions of the Zhang-Rice $S=1/2$ spins $\widetilde{\mathbf{S}}_j$ and $P_{j,j\pm2\delta}$ permutes $\widetilde{\mathbf{S}}_j$ with its nearest $S=1$ spins $\mathbf{S}_{j\pm2\delta}$. The resulting values of t and J' are $t = 0.36t_1 + 1.027t_2 \sim 1eV \sim 40J$, and $J' = 0.18J_K \sim 0.25eV$, in agreement with simple expectations[13,19]. The $S(\pi, \omega)$ obtained using H_{1b} is very different from that of H_{sf} and displays only one peak (around 6meV) below the Haldane gap. This result is in fact more similar to the response of the undoped system.
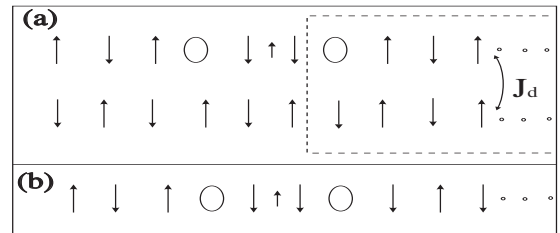

FIG. 2. (a) Top: schematic representation of the ground state of H_{ef} for one added O hole (indicated by the small up arrow). The dashed line indicates a region in which the interchain interactions J_d are frustrated due to the change of the interchain short-range magnetic correlations produced by the O hole. (b)The same for the first excited state. The Ni states with $S^z = 1, 0, -1$ are indicated by $\uparrow$, 0, $\downarrow$ respectively.

To shed light onto the underlying physics, it is instructive to solve H_{sf} in a Ni_3O_2 chain. The ground state has $S=5/2$ and is nearly degenerate to an $S=3/2$ state. Except for the parity of the wave functions, the result can be interpreted as if the central static ZRD were strongly FM coupled to one of the neighboring Ni spins and very weakly FM coupled to the other one. This quasidegeneracy is not obtained with H_{1b} for any set of parameters, indicating that the inclusion of quadruplets is crucial to have this weak link. This image is confirmed by the analysis of the dominant terms in the wave function of the ground and first excited states represented in Fig. 2, and provides a plausible explanation of the susceptibility measurements of Kojima *et al.*[8]: at temperatures above the effective exchange of the weak link, the chains behave as being cut, and a segment between two ZRD's can have zero, one or both ZRD's FM coupled with it, with probabilities $1/4$, $1/2$ and $1/4$ respectively. If the number of Ni atoms in the segment is even, the spin of the segment is zero. Then, the corresponding total spin of the segment plus coupled ZRD's is 0, 1/2, 0 for the three cases respectively. If the number of sites in the segment is odd, the spin of the segment is equal to 1 and the corresponding total spin is 1, 3/2 and 2 respectively. This gives an average $\langle S(S+1) \rangle = 17/8$ in excellent agreement with the observed Curie constant[8].

An important feature of the ground (first excited) state of H_{sf} in the 10-site chain, is that the end spins display FM (AFM) correlations. When the interchain exchange J_b is included, this implies that for 10% Ca doping, near five Ni spins have the wrong sign of the magnetic correlations with neighboring chains, implying a frustration energy of roughly $20J_b = 3.2K$ (see Fig. 2). Since this energy is within the order of magnitude of the randomly (due to disorder[7]) distributed lowest excitation energies, a spin glass behavior with characteristic temperatures near $3K$ is expected, in agreement with experiment[8].

In summary, starting from a multiband Hamiltonian similar to a one used previously for NiO[20] but including only $3d$ e_g orbitals, we have derived a low-energy Hamiltonian for doped Y_2BaNiO_5, and used it to understand magnetic properties of the Ca doped system, particularly the additional states inside the Haldane gap. Contrary to previous predictions[12], we obtain that these states are quite different to these produced by Zn doping and substantial weight near the middle of the Haldane gap is obtained only for Ca doping.

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